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(54) Process for manufacturing organoclays having enhanced gelling properties.

(57) A process is disclosed for preparing an improved organoclay having enhanced gelling properties by reacting a smectite-type clay with a higher alkyl-containing quaternary ammonium compound, the improvement being effected by subjecting the clay to high-speed fluid shear as a pumpable slurry or to high energy pugmilling prior to the reaction thereof with the higher alkyl-containing quaternary ammonium compound.

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PROCESS FOR MANUFACTURING ORGANOCLOYS HAVING ENHANCED GELLING PROPERTIES

Background of Invention

This invention relates generally to organophilic clays (hereinafter referred to as "organoclays"), and more specifically relates to an improved process for manufacture of same, which process strikingly enhances the gelling properties of the said products.

Organoclays, representing the reaction product of a smectite-type clay with a higher alkyl-containing quaternary ammonium compound, have long been known for use in gelling of organic liquids such as lubricating oils, linseed oil, toluene and the like. A large variety of highly useful products, such as lubricating greases are producible through use of such gelling agents. The procedures and chemical reactions pursuant to which these organoclays are prepared, are well-known. Thus, under appropriate conditions, the organic compound which contains a cation, will react by ion exchange with clays which contain a negative layer lattice and exchangeable cations to form the organoclay products. If the organic cation contains at least one alkyl group containing at least 10 carbon atoms, then the resultant organoclays will have the property of swelling in certain organic liquids.

Among the prior art patents which discuss at length aspects of the preparation and properties of organoclays, as above outlined, are U.S. Patents No. 2,531,427; 2,966,506; 3,974,125; 3,537,994; and 4,081,496. Reference may also be had to applicable portions of the standard reference work "Clay Mineralogy", 2nd Edition, 1968, by Ralph E. Grim, McGraw Hill Book Company.

In the usual procedure for preparing an organophilic clay pursuant to this prior art, the smectite-type clay, selected, quaternary compound and water are mixed together, preferably at an elevated temperature, typically in the range of 100°F to 180°F, for a period of time sufficient for the organic quaternary ammonium compound to coat the clay particles. Thereafter, the product can be filtered, washed, dried and ground, or otherwise processed, depending upon the intended use. In some instances, e.g., the drying and grinding step may be omitted. Various other modifications of this process may be used depending upon the form of product desired --as will be noted in the referenced patents.

Summary of Invention

Now in accordance with the present invention, it has unexpectedly been discovered that the known process for manufacture of an organoclay, wherein a smectite-type clay is reacted with a higher alkyl-containing quaternary ammonium compound, may be improved to yield striking enhancement of the gelling properties of the resultant organoclay product, by subjecting the clay as a pumpable slurry to high speed fluid shear, or alternatively to high energy pugmilling, prior to the said reaction thereof with the ammonium compound. High energy pugmilling is preferably effected by extruding the clay at 25 to 40 weight percent moisture content, through a pugmill which imparts at least 20 HP-hr/ton dry clay of energy to the clay.

While we are aware of cursory reference in U.S. Patents Nos. 4,081,469 and 4,116,866 to use of a pug mill or extruder for shearing an aqueous clay slurry, in order to facilitate a reaction wherein a bentonite-type clay is to be converted to sodium form, by reaction with a soluble sodium compound, we are not aware of any use of high speed fluid shear or pugmilling for treating the clay prior to reaction with a quaternary amine, for improving the gelling properties of the resultant organoclay.

The high speed fluid shear to which the smectite-type clay is subjected in accordance with one aspect of the process of this invention, is effected by passing the pumpable slurry through a dispersion or colloid mill, which devices are often referred to in the art as "homogenizers". Dispersion and colloid mills are thus well-known in the art, and are succinctly discussed and characterized at pages 842 and 843 of "Chemical Engineers Handbook", edited by R. H. Perry and C. H. Chilton, 5th Edition, 1973, McGraw Hill Book Company (New York). As is pointed out in this standard reference work, this type of device constitutes a special class of mills normally employed for dispersion and colloidal operations. Such mills operate on a principle of high speed fluid shear. Preferred mills for use in the invention are characterized by including or defining a narrow gap across which a pressure differential is maintained and through which in accordance with the invention the pumpable slurry is passed.

Preferably, the high speed fluid shear is effected by passing the slurry at high velocities through a narrow gap, across which a high pressure differential is maintained. This type of action, e.g., can be effected in the well-known Manton-Gaulin mill, which device is sometimes referred to as the "Gaulin homogenizer". In the basic operation of such device, a reciprocating, positive displacement piston-type pump is provided with a homogenizing

valve assembly which is affixed to the pump discharge. The unhomogenized product enters the valve area at high pressure and low velocity. As it passes through a narrow orifice at the valve, (which is a close-clearance area between the valve and valve seat), its velocity is increased to levels approaching sonic. This provides high shear forces for reduction, and in the said device, these forces are further implemented as this high velocity stream strikes an impact ring where its direction is changed. Of further interest in this connection, is U.S. Patent No. 3,348,778, to M. I. Chin et al, which discloses the use of a Manton-Gaulin type arrangement for treating kaolin clays in order to improve the rheology of a clay-water system subsequently formed from same. For present purposes, the patent is of interest in disclosing certain useful arrangements for the said mill, and further details of the construction of same. The patent also discusses the gap provided in the mills of the type disclosed, and properly observes that such gap is only a fraction of an inch, usually of the order of .001 to .005 inch, but under certain conditions may be as large as 0.09 inch or even 0.1 inch.

In those instances where a gap arrangement, as in the Manton-Gaulin mill, is utilized, the said pressure differential across the gap is preferably in the range of from 1000 to 8000 p.s.i.g. with 4,000 to 6,000 p.s.i.g. being more typical in representative operations. Depending upon the specifics of the equipment, pressures higher than 8,000 p.s.i.g. can readily be used.

The said slurry will typically include less than 25% by weight of solids; however, the solids content can vary, and be above the indicated level if appropriate dispersing agents are present. The principal requirement is that the slurry indeed be pumpable, so that it is capable of being subjected to the aforementioned high speed fluid shear.

In addition to the passage through a narrow gap, as in the aforementioned type Manton-Gaulin mill, the high speed fluid shear can also be effected, pursuant to the invention, by use of dispersion and colloid mills based upon a stator and a closely spaced rotor, wherein a high speed rotation is maintained between the two said elements. The slurry in this instance is subjected to the high speed fluid shear by being passed through the gap between the stator and the rotor. The well-known Greer mill is one example of this type of construction, and may be utilized as one instrumentality in practice of the invention. In the said Greer mill a narrow gap is defined by a stationary stator and a rotor which rotates within the vertically surrounding stator. The slurry to be treated in accordance with the invention is passed through that gap under pressure.

Further instrumentalities useful in effecting high speed fluid shear are discussed in the aforementioned reference to Perry and Chilton.

Alternatively, the smectite-type clay is subjected in accordance with the process of this invention, to high energy pugmilling, which is preferably effected by passing the smectite-type clay through a pugmill of the type disclosed in U.S. Patent No. 3,574,345. Such device includes a barrel, a motor driven screw mounted in the barrel, and apertured plates at the tapered output end of the barrel from which the material worked in the pugmill is extruded. The said pugmill differs especially from conventional pugmills in having an L/D ratio of from 4:1 to 10:1, where L is the effective length of the screw or auger in the barrel of the pugmill, and D is the internal diameter of the portion of the barrel containing the screw.

It is preferable in accordance with the invention, to impart at least 40 to 50 HP-hr energy per ton of dry clay to the material passing through the pugmill. Higher levels of energy may also be usefully imparted, although this may require multiple passes through the pugmill.

The precise manner in which the high energy treatment in accordance with the invention acts to enable the remarkable improvements in gelling properties is not fully understood. Among other things, however, it has been found that such treatment has a marked effect on the average particle size of the clay. It, thus, has been determined that where a bentonite-type feed sample having an average particle size of 0.756 microns is passed through a Manton-Gaulin mill where the energy input was 210 HP-hours per ton of clay, the average particle size was reduced to 0.438 micrometers. In a second instance, the average particle size of the clay was reduced from 0.756 micrometers to 0.352 micrometers when the energy input was 700 horsepower hours per ton of clay. Similar reductions in average particle size are achieved when the clay is passed through a pugmill of the type above described. Thus, for example, when a smectite-type clay having an average particle size of 0.475 micrometers is passed through such a pugmill and approximately 30 HP-hr/ton clay of energy is dissipated therein, the average particle size is reduced to 0.391 micrometers. At energy dissipation levels of 51 and 108 HP-hr/ton, a feed clay having an average particle size of 0.756 micrometers is so changed that the particle size is reduced to 0.277 and 0.276 micrometers, respectively. This data indicates a very substantial average particle size reduction, and is one consequence of the treatment of the clay. (These data are weight average particle size of the bentonite dispersed in water, as measured on a "Nanosizer" apparatus marketed by Coulter).

The smectite-type clays which are subjected to the improved process of this invention, are precisely those which have been conventionally utilized in the prior art in the preparation of organoclays as aforementioned. These are smectite-type clays which have a cation exchange capacity of at least 75 milliequivalents per 100 grams of clay. Useful clays for such purposes include the naturally occurring Wyoming variety of swelling bentonite and similar clays, and hectorite, which is a swelling magnesium-lithium silicate clay. The clays are preferably converted to the sodium form if they are not already in this form. This can be effected, again as is known in the art, by a cation exchange reaction, or the clay can be converted via an aqueous reaction with a soluble sodium compound.

Smectite-type clays prepared synthetically can also be utilized, such as montmorillonite, bentonite, beidelite, hectorite-saponite, and stevensite.

In a typical procedure pursuant to the invention, the crude smectite-type clay, as for example a bentonite, is initially dispersed in water at relatively low solids, typically at less than 10% by weight. The slurry is then screened and centrifuged to remove non-clay components and especially abrasive elements such as quartz. Removal of these abrasive elements is especially preferred if the slurry is thereupon to be subjected to shearing forces as by passing through a narrow gap as in the Manton-Gaulin mill. Were such abrasives present, the orifice channel and attendant portions of the mill would rapidly become damaged.

The fine fraction from the centrifuge, which typically includes 4 to 5% solids, is then subjected to high speed fluid shear in accordance with the invention. Typically, as aforementioned, the said slurry may be passed through a Manton-Gaulin homogenizer in which pressures of 1000 to 8000 p.s.i.g. are maintained across the gap, and pressures of 4000 to 6000 p.s.i.g. are typical. The output clay product from the high speed fluid shear step is then subjected to the conventional reaction with the quaternary amine.

Alternatively, the crude smectite-type clay is adjusted with water to approximately 60.0 to 75.0% solids. The crude is then passed through a pugmill under conditions which impart at least 40 to 50 HP-hr energy per ton of dry clay. In the event the crude is not a sodium clay, sodium carbonate may be added during the pugmilling process to produce a sodium bentonite. The clay is then dispersed in water at relatively low solids, typically at less than 10% by weight. The slurry is then screened and centrifuged to remove non-clay components and especially abrasive elements such as quartz. The centrifuge is preferably set to recover a less than 4 micron cut, as is usual in preparing the clay for the organic reaction.

The fine fraction from the centrifuge is then subjected to the conventional reaction with the quaternary amine.

The reaction of the high speed fluid-sheared or pugmilled clay with the amine is effected by the conventional procedures described at great length in the prior art, including in the previously mentioned patents.

The organic compounds which are reacted with the treated clay are quaternary ammonium salts, where the salt anion is preferably chloride or bromide or mixtures thereof; and is more preferably chloride ion. The salt anion may also, however, be nitrate, hydroxyl, acetate, or mixtures of these. Any of such compounds as are known to be useful in producing organoclay gellants of the type herein discussed may be used in this aspect of the invention, specifically including the compounds so reported useful in the patents heretofore cited. Among others these include dimethyl di-(hydrogenated tallow), dimethyl benzyl hydrogenated tallow, dibenzyl dialkyl, methyl benzyl dialkyl, and trimethyl hydrogenated tallow salts.

Pursuant to the improvements yielded by the invention, the gelling characteristics i.e. the gelling efficiency of the clays treated by the invention, are so markedly enhanced, as to make possible use of quantities of the gelling agent to achieve a given result, which are reduced in comparison to the amount which would be required in the absence of the invention. Further clays, such as certain deposits of bentonite-type clays which heretofore had been considered unacceptable as crude materials for use in preparing suitable gellants, are found when treated by the process of the invention, to yield organoclay gelling agents which are fully acceptable for use in gelling organic liquids or the like. A net effect of the invention in this regard, is therefore to enable highly effective use of crude deposits previously deemed usable for these purposes, thereby vastly expanding the possible sources of raw materials which can be used to produce the final gellant products.

Brief Description of Drawings

In the drawings appended hereto:

FIGURE 1 is a graph comparing the effects of gelling a diesel fuel with an organoclay prepared by the process of the invention, with an organoclay which has been conventionally processed;

FIGURE 2 is a graph similar to Figure 1 and illustrating the comparative results achieved where an organoclay in accordance with the invention, and a control untreated organoclay, are each used in the gelling of odorless mineral spirits;

FIGURE 3 is a further graph similar to the foregoing graphs, and illustrating comparable data for a toluene gel.

FIGURE 4 is a further graph of the same character as the prior graphs, illustrating gelling effects in a further odorless mineral spirits, where the starting crude clay is of relatively poor quality;

FIGURE 5 is a graph of the same character as in Figure 4, but illustrating comparative data for viscosity measurements of a toluene gel;

FIGURE 6 is a further graph illustrating test data for a gelled diesel fuel as in prior Figures, except in this instance a further type of high speed fluid shearing is effected;

FIGURE 7 is similar to Figure 6, but shows the gelling improvement achieved in odorless mineral spirits through use of shearing as in the data for Figure 6;

FIGURE 8 is a graph comparing the effects of gelling a diesel fuel with a bentonite slurry prepared by an alternative embodiment of the process of the invention, with a bentonite slurry which has been conventionally processed;

FIGURE 9 is a graph similar to Figure 8 and illustrating the comparative results achieved where an organoclay in accordance with the invention, and a control untreated clay, are each used in the gelling of odorless mineral spirits; and

FIGURE 10 is a further graph similar to the foregoing graphs, and illustrating comparable data for a toluene gel.

Description of Preferred Embodiments

The invention will now be illustrated by a series of Examples, which are intended to set forth typical and preferred procedures to be utilized in practice of the process of the invention.

Example I

In this Example, the smectite-type clay utilized as a starting material was a Wyoming bentonite. The crude bentonite was initially dispersed in water at 7% solids by weight. The slurry was thereupon screened, and then centrifuged to remove non-clay components and especially abrasive elements such as quartz. The fine fraction from the centrifuge, which then included approximately 4 to 5% solids by weight, was divided into two portions. One such portion served as a control sample. The second portion, in accordance with the invention, was passed through a Manton-Gaulin homogenizer, wherein pressures of 5000 p.s.i.g. were maintained across the gap of the said apparatus. The control and the sheared samples, were each divided into

further portions, which were reacted with the salt of a dimethyl di(hydrogenated tallow) amine. The ratio of amine to clay was varied in the samples from 85 to 105 milliequivalents per 100 grams of clay on a 100% active clay basis. The amine was stirred into the approximately 4 to 5% solids slurry at 60°C, with stirring being continued for approximately 1/2 hour, after which the material was filtered, washed with water and dried at 60°C. The dried material was pulverized with a Mikropul mill to approximately 95% less than 200 mesh. Tests were then conducted to determine the gelling properties of each of the control and invention samples.

In Figure 1 herein, Fann viscosity in cps is plotted as a function of milliequivalents of the amine added to the clay for the untreated bentonite samples, i.e., the prior art samples, and for the sample treated in accordance with the invention. - (Loss on ignition is also plotted as abscissa, which is a measure of the organics combined with the clay). The type of bentonite utilized in this example is considered by those skilled in the art to be relatively "good" for use in preparing organoclay gellants. Viscosity measurements were effected by measuring a quantity of diesel oil into a multi-mixer can. In each instance, the sample to be evaluated was added to the diesel oil with stirring, after which water was stirred into the mix, the can removed from the mixer, and placed on the Fann viscometer, and the 600 and 300 rpm readings obtained. Gel readings were obtained after 10 seconds. It will be apparent that a vast improvement in viscosity of the gelled diesel fuel is evidenced across all ranges of the amine-to-clay ratio where the method of the invention is used.

Example II

In this instance, the same procedure was utilized as in Example I, except that the effect of the invention on the gellant were evaluated by admixing same with odorless mineral spirits (OMS). In the said procedure, a fixed quantity of the odorless mineral spirits were transferred to a container and the temperature is established for same. A small quantity of 100% propylene carbonate was added to the mixture, while stirring. Next, a specified quantity of the sample to be evaluated was transferred to the container, followed by vigorous stirring. The mixture was blunged with a Cowles blade for two minutes and the gel stirred for 10 revolutions with a spatula. The container was covered and the gel allowed to remain in a constant temperature bath at 24°C, + or -1°C for two hours, after which the gel viscosity was measured on a Brookfield viscometer. The resulting data is plotted in Figure 2, and establishes even a more remark-

able difference between the treated and untreated organoclays with respect to their ability to gel the said odorless mineral spirits.

Example III

In Figure 3, the same material as in Examples I and II, resulting from the present invention is evaluated for its gelling characteristics in toluene. In this procedure, 6 grams of the organoclay was admixed with 340 ml of toluene by use of a Waring blender. 2.3 ml of a polar dispersant was then added, consisting of 95% by weight methanol and 5% by weight of deionized water, and additional blending carried out. (In general, small proportions of polar compounds may be added to develop maximum viscosity. Typical polar activators are water, methanol, and propylene carbonate). The contents were then poured into a container, allowing the gel to flow very thinly over the container lip, thus allowing any air bubbles to escape. The container was maintained in a water bath at 74°C + or -1°F, for two hours, after which Brookfield viscosity readings were obtained. Once again, Figure 3 illustrates the striking improvements yielded by practice of the invention.

Example IV

In this Example, the same procedure was utilized as in Example I for purposes of preparing the modified bentonite, except the bentonite sample utilized herein differed from that in Example I in being a crude of a type normally regarded as "poor" for producing an organoclay gelling agent. The same procedures as aforementioned were used in treating odorless mineral spirits. The data yielded is set forth in Figure 4. It is clear that the process of the invention has yielded a remarkable increase in gelling capacity for the material treated by the invention. Indeed, as mentioned, the said bentonite crude would, where processed by conventional techniques, be regarded as an unacceptable gellant, whereas the organoclay yielded by the process of the invention is a completely acceptable product.

Example V

In this Example, a further so-called "poor" bentonite was processed in accordance with the invention and in accordance with prior art, and the effects upon gelling of toluene were established by the procedures of Example III. The graphical showing of Figure 5 illustrates the same consequences,

as discussed for Example IV; i.e., that by the process of the invention, a remarkable improvement in the gelling properties of an otherwise poor bentonite have been achieved, resulting in a highly usable material in place of a material which heretofore was unacceptable for preparation of organoclays intended for use as gelling agents.

Example VI

In this Example, samples of a further refined bentonite slurry which was initially processed as described in connection with Example I, was subjected to high speed fluid shear by being passed through a Greer mixer, which is a well-known dispersion mill of the rotor/stator type. In this procedure, the slurry was mixed with the Greer for a minimum of 5 minutes at maximum speed, 8500 rpm. Directly after mixing, the amine was added in the normal manner. The comparative data yielded depicts gelling effects in a diesel fuel for samples treated by the invention, vis-a-vis samples conventionally processed. These show a good improvement where the process of the invention is utilized, although the improvement is not so marked as that yielded where the Manton-Gaulin type of mill is used.

Example VII

In this Example, the procedure described in Example VI was followed, except that the resulting samples were evaluated for use in gelling odorless mineral spirits. The resultant data is set forth in Figure 6. Again, it is seen that the process of the invention results in marked improvements, although these again are not so striking as those yielded where the slurry is passed through the Manton-Gaulin type of processing.

Passage of the clay slurry through a narrow pressurized gap in accordance with the invention yields results that differ fundamentally from what occurs where a conventional blade or disc-type mixer such as a Waring Blender or a Cowles disperser is utilized. This can be appreciated by comparing the shearing mechanisms imposed upon a fluid in a Cowles high speed disperser with those imposed by the Manton-Gaulin mill.

In the Cowles high speed dissolver shear is imposed upon a fluid by smashing actions of the blades (mechanical energy) and by smearing arising from laminar flow. Of the two, the smearing mechanism is the more important, and the efficiency of dispersion is determined by the stirring design configuration (RPM, blade size, container size and shape). Swirling, turbulent flow creates

efficient mixing but most significantly, intermingled pockets remain undispersed. Conversely, the laminar flow pattern may fail to provide efficient mixing, but the drag of layers over each other tears any clumps of particles apart, and efficient dispersion is obtained. Additionally, the more viscous the fluid, the more effective is the tearing, and the efficiency of the Cowles disperser increases with increasing viscosity.

In contrast, the Manton-Gaulin mill allows the product to enter an expansion valve at a very high pressure and low velocity. As the product enters the close clearance area between the valve and the valve seat there is a rapid increase in velocity to the order of 30,000 cm/sec with a corresponding decrease in pressure arising from the Bernoulli effect. This allows the formation of bubbles which implode with extreme energy as the product velocity decreases upon leaving the valve seat area. This promotes the creation of shock waves which induce shearing by collision; this process is known as cavitation. In contrast to the behaviour of the Cowles apparatus, the efficiency of the Manton-Gaulin mill decreases with increasing viscosity arising from rapid dissipation of shear waves.

It can be shown the the shear stress in a typical Cowles dissolver is approximately 2013 dynes/cm². (This assumes a fluid density of 1.0 g/cm³ and a circular rim blade velocity of 4000 ft/min (2000 cm/sec) for a dissolver with a .4 inch blade.

Although the Manton-Gaulin mill does not employ laminar flow as a shearing mechanism, assuming a laminar model may give an upper bound to the shear rate and shear stresses encountered upon cavitation. Because of the extreme pressure shearing of the order of magnitude of laminar stress may be encountered.

Assuming this and a reasonable distance between the valve and valve seat (100 microns) a shear rate may be estimated from manufacturer specifications as about $2.9 \times 10^6 \text{ sec}^{-1}$. The shear stress can then be shown to be $8.8 \times 10^7 \text{ dynes cm}^{-1}$.

From the foregoing it may be concluded that the following differences exist between the Cowles and Manton-Gaulin devices:

1. The Manton-Gaulin mill operates on the principle of cavitation involving extremely high particle velocities and turbulent flow. The Cowles apparatus operates at low shear rates with efficient dispersion arising from laminar flow.

2. The efficiency of the Cowles disperser increases with increasing viscosity; that of the Gaulin apparatus decreases.

3. Clay particles in suspension experience much higher shear stresses and shear rates in the Gaulin apparatus, although these are not amenable to direct calculation.

4. In order to compare the total shear exerted upon a clay slurry per unit area, time integrals must be compared. Assuming the Gaulin apparatus has a pump stroke of 1800 RPM (.03 sec/stroke) the total shear time values can be estimated, and indicate that a 35 minutes shear in the Cowles device typically equates to one pump stroke on the Manton-Gaulin apparatus insofar as total shear is concerned.

Example VIII

In this Example, the smectite-type clay utilized as a starting material was a Wyoming bentonite. The crude bentonite was adjusted with water to approximately 60 to 75% solids, and was then passed through a pugmill of the type disclosed in the aforementioned 3,574,345 patent. The mill had an L/D ratio of about 7.5:1. Approximately 40 to 50 HP-hr/ton of dry clay of energy was imparted to the materials. The pugged bentonite was thereupon dispersed in water at 7% solids by weight. The slurry was thereupon screened, and then centrifuged to remove non-clay components, including abrasive elements such as quartz. The fine fraction from the centrifuge then included approximately 4 to 5% solids by weight. The treated samples were divided into further portions which were reacted with the salt of a dimethyl di(hydrogenated tallow) amine. The ratio of amine to clay was varied in the samples from 85 to 105 milliequivalents per 100 grams of clay on a 100% active clay basis. The amine was stirred into the approximately 4 to 5% solids slurry at 60°C, with stirring being continued for approximately 1/2 hour, after which the material was filtered, washed with water and dried at 60°C. The dried material was pulverized with a Mikropul mill to approximately 95% less than 200 mesh. Tests were then conducted to determine the gelling properties of each of the invention samples.

In Figure 8 herein, Fann viscosity in cps is plotted as a function of milliequivalents of the amine added to the clay for untreated bentonite samples, i.e., the prior art samples, and for the sample treated in accordance with the invention. - (Loss on ignition is also plotted as abscissa, which is a measure of the organics combined with the clay). The type of bentonite utilized in this example is considered by those skilled in the art to be relatively "good" for use in preparing organoclay gellants. Viscosity measurements were effected by measuring a quantity of diesel oil into a multi-mixer can. In each instance, the sample to be evaluated

was added to the diesel oil with stirring, after which water was stirred into the mix, the can removed from the mixer, and placed on the Fann viscometer, and the 600, and 300 rpm readings obtained. Gel readings were obtained after 10 seconds. It will be apparent that a vast improvement in viscosity of the gelled diesel fuel is evidenced across all ranges of the amine-to-clay ratio where the method of the invention is used.

Example IX

In this instance, the same procedure was utilized as in Example VIII, except that the effect of the invention on the gellant were evaluated by admixing same with odorless mineral spirits (OMS). In the said procedure, a fixed quantity of the odorless mineral spirits were transferred to a container and the temperature is established for same. A small quantity of 100% propylene carbonate was added to the mixture, while stirring. Next, a specified quantity of the sample to be evaluated was transferred to the container, followed by vigorous stirring. The mixture was blunged with a Cowles blade to two minutes and the gel stirred for 10 revolutions with a spatula. The container was covered and the gel allowed to remain in a constant temperature bath at 24°C, + or -1°C for two hours, after which the gel viscosity was measured on a Brookfield viscometer. The resulting data is plotted in Figure 9, and establishes even a more remarkable difference between the treated and untreated organoclays with respect to their ability to gel the said odorless mineral spirits.

Example X

In Figure 10, a similar material to that used in Examples VIII and IX, resulting from the present invention, is evaluated for its gelling characteristics in toluene. In this procedure, 6 grams of the organoclay was admixed with 340 ml of toluene by use of a Waring blender. 2.3 ml of a polar dispersant was then added, consisting of 95% by weight methanol and 5% by weight of deionized water, and additional blending carried out. (In general, small proportions of polar compounds may be added to develop maximum viscosity. Typical polar activators are water, methanol, and propylene carbonate). The contents were then poured into a container, allowing the gel to flow very thinly over the container lip, thus allowing any air bubbles to escape. The container was maintained in a water bath at 74° + or -1°F, for two hours, after which Brookfield viscosity readings were obtained. Once

again, Figure 10 illustrates the striking improvements yielded by practice of the invention.

While the present invention has been particularly set forth in terms of specific embodiments thereof, it will be understood in view of the instant disclosure, that numerous variations upon the invention are now enabled to those skilled in the art, which variations yet reside within the scope of the present teaching. Accordingly, the invention is to be broadly construed, and limited only by the scope and spirit of the claims now appended hereto.

Claims

1. A process for the manufacture of an organoclay having enhanced gelling properties by reacting a smectite-type clay with a higher alkyl-containing quaternary ammonium compound, the invention characterized in that the clay is subjected to high speed fluid shear as a pumpable slurry or to high energy pugmilling prior to said reaction thereof with said ammonium compound.

2. The process according to claim 1 characterized in that said pumpable slurry of clay is subjected to high speed fluid shear by passing said slurry through a narrow gap across which a pressure differential is maintained.

3. A method in accordance with claim 2, characterized in that said high speed fluid shear includes impacting the clay at a high velocity beyond said gap, against a hard surface to effect further shearing and comminution of said clay particles.

4. A method in accordance with claim 2, characterized in that pressure differential is in the range of 1,000 to 8,000 p.s.i.g.

5. A method in accordance with claim 2, characterized in that pressure differential is in the range of 4,000 to 6,000 p.s.i.g.

6. A method in accordance with any one of claims 1, 2, 3 or 4 characterized in that said shearing and impacting is effected in a homogenizing mill.

7. A method in accordance with claim 6, characterized in that said pumpable slurry includes less than 25% by weight of solids.

8. A method in accordance with claim 6, characterized in that said fluid shear is effected by passing said slurry through a dispersion mill including a stator and a rotor closely spaced therefrom and rotated at a high speed with respect thereto, said slurry being subjected to said shearing forces in at least the gap between the stator and rotor.

9. A method in accordance with claim 1, characterized in that said high energy pugmilling is effected by passing said clay while moist through a pugmill which imparts at least 20 HP-hrs/ton of energy to the moist clay.

10. A method in accordance with claim 9, characterized in that said clay is passed through said pugmill at 25 to 40 weight percent moisture content.

11. A method in accordance with claim 10, characterized in that said imparted energy is at least 40 HP-hr/ton.

12. A method in accordance with claim 9, characterized in that said pugmill has an L/D ratio of from about 4:1 to 10:1.

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30

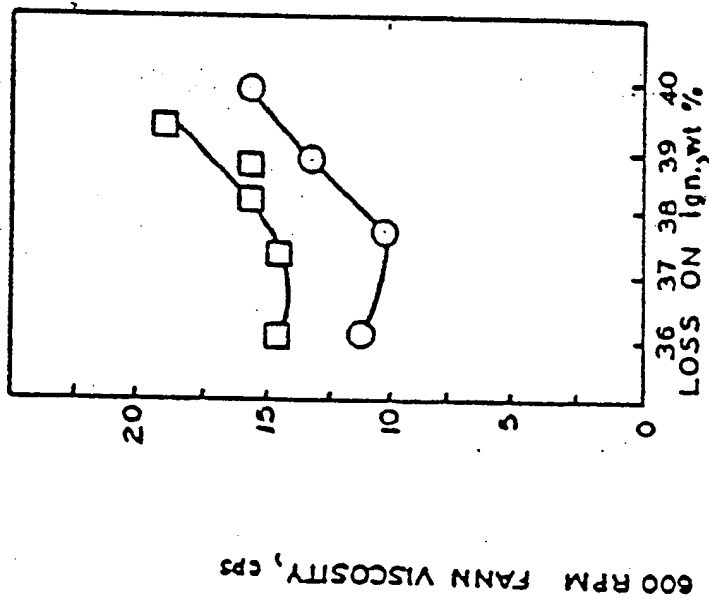
35

40

45

50

55



○ UNTREATED (GOOD BENTONITE)
 □ TREATED

FIG. 1

EFFECT OF TREATMENT OF REFINED BENTONITE SLURRY BY INVENTION. VISCOSITY MEASURED IN DIESEL FUEL GEL.

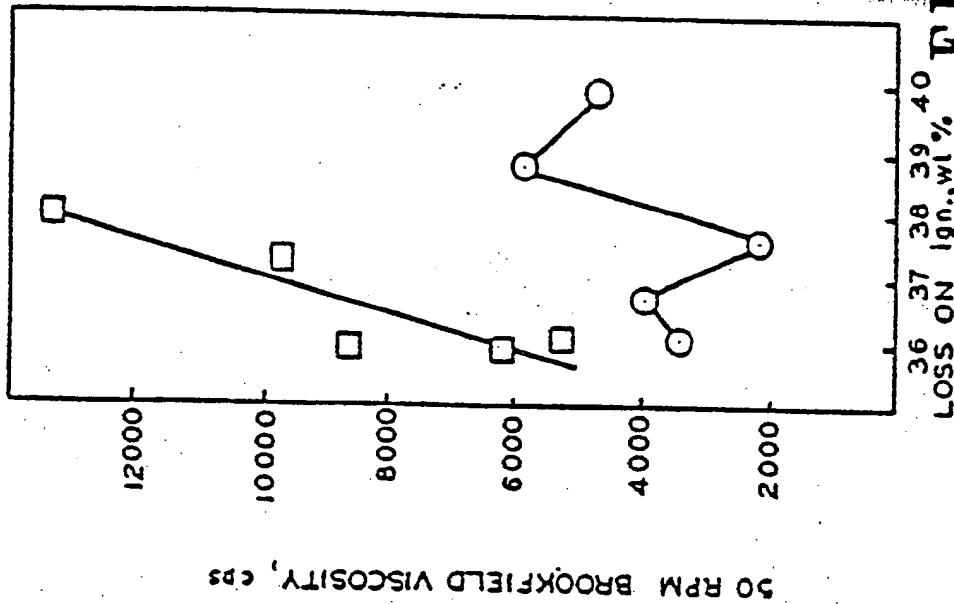
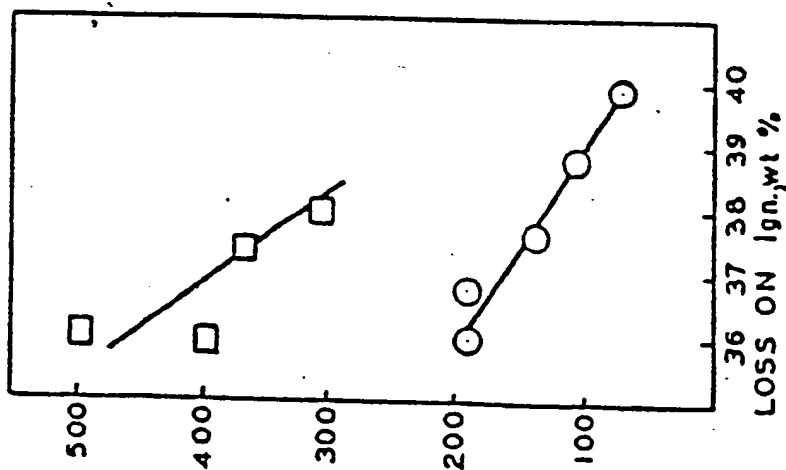


FIG. 2

○ UNTREATED (GOOD BENTONITE)
 □ TREATED

EFFECT OF TREATMENT OF REFINED BENTONITE SLURRY BY INVENTION. VISCOSITY MEASURED IN ODORLESS MINERAL SPIRIT GEL.

50 RPM BROOKFIELD VISCOSITY, cps



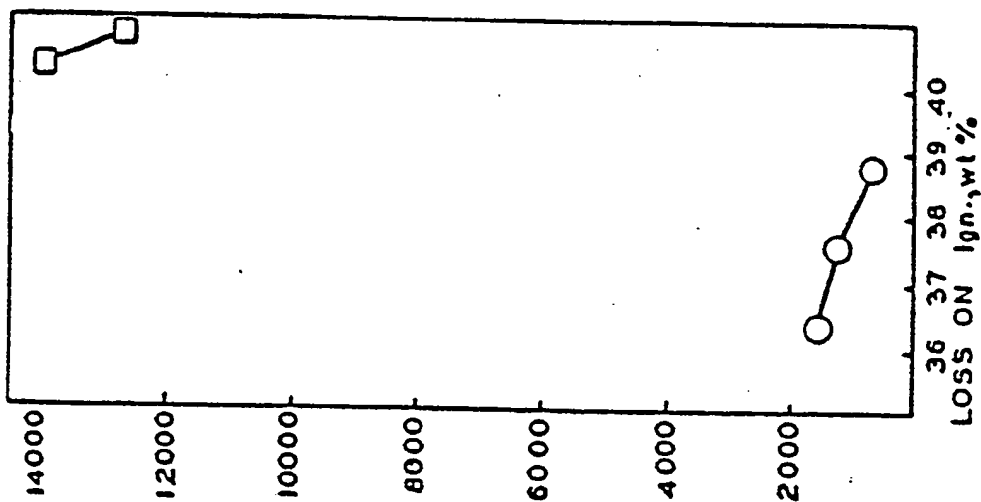
AMINE/CLAY, mg / 100g

UNTREATED (GOOD BENTONITE)

TREATED

FIG. 3

EFFECT OF TREATMENT OF REFINED BENTONITE SLURRY BY INVENTION. VISCOSITY MEASURED IN TOLUENE GEL.



LOSS ON IGN., WT %

AMINE/CLAY, mg / 100g

UNTREATED (POOR BENTONITE)

TREATED

FIG. 4

EFFECT OF TREATMENT OF REFINED BENTONITE SLURRY BY INVENTION. VISCOSITY MEASURED IN ODORLESS MINERAL SPIRIT.

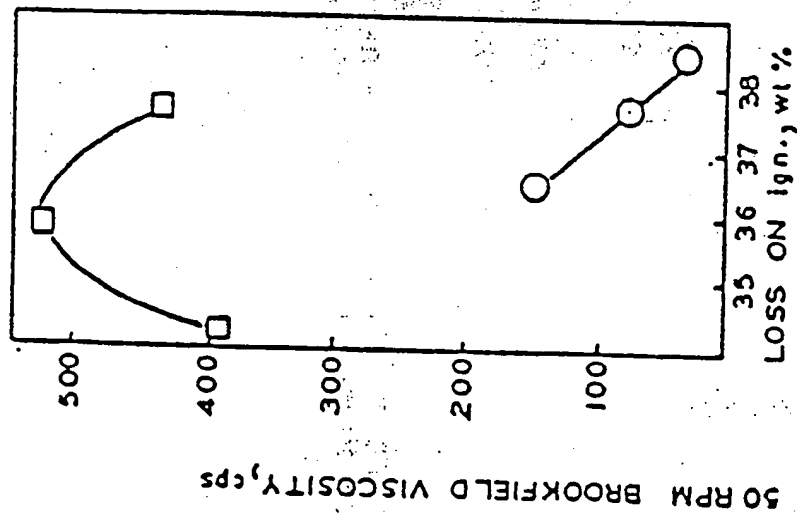


FIG. 5

EFFECT OF TREATMENT OF REFINED BENTONITE BY INVENTION. VISCOSITY MEASURED IN TOLUENE GEL.

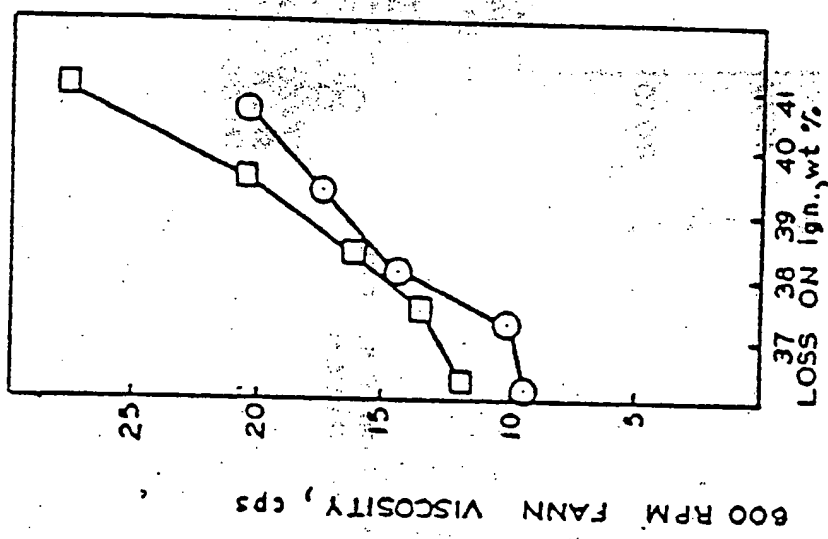


FIG. 6

EFFECT OF TREATMENT OF REFINED BENTONITE SLURRY BY A ROTOR/STATOR MIXER. VISCOSITY MEASURED IN DIESEL FUEL.

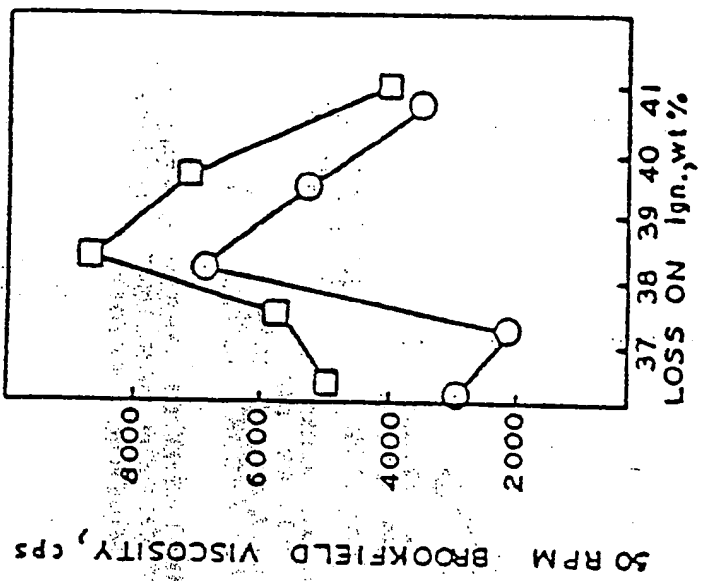


FIG. 7

EFFECT OF TREATMENT OF REFINED BENTONITE SLURRY BY A ROTOR/STATOR MIXER. VISCOSITY MEASURED IN ODORLESS MINERAL SPIRIT.

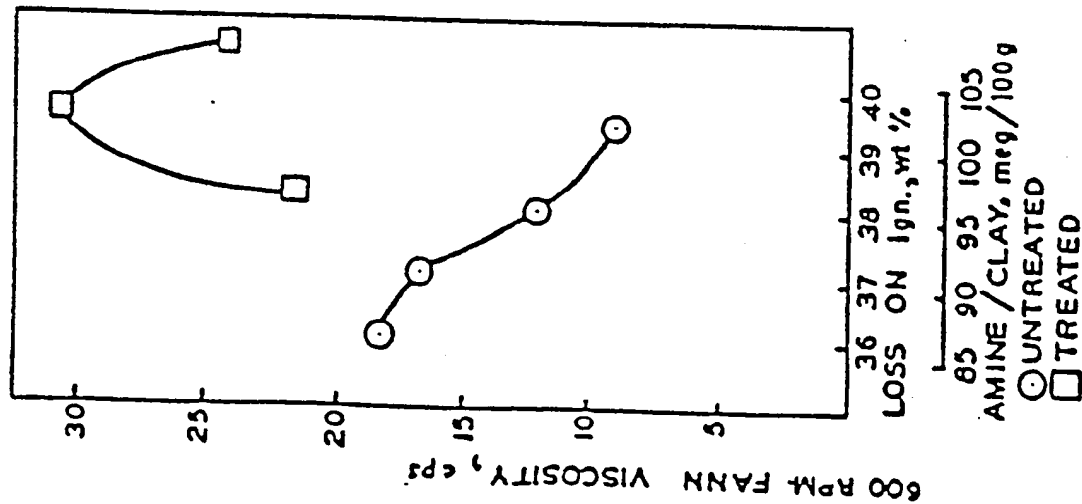


FIG. 8

EFFECT OF TREATMENT OF CRUDE BENTONITE BY HIGH ENERGY PUGMILLING. VISCOSITY MEASURED IN DIESEL FUEL GEL.

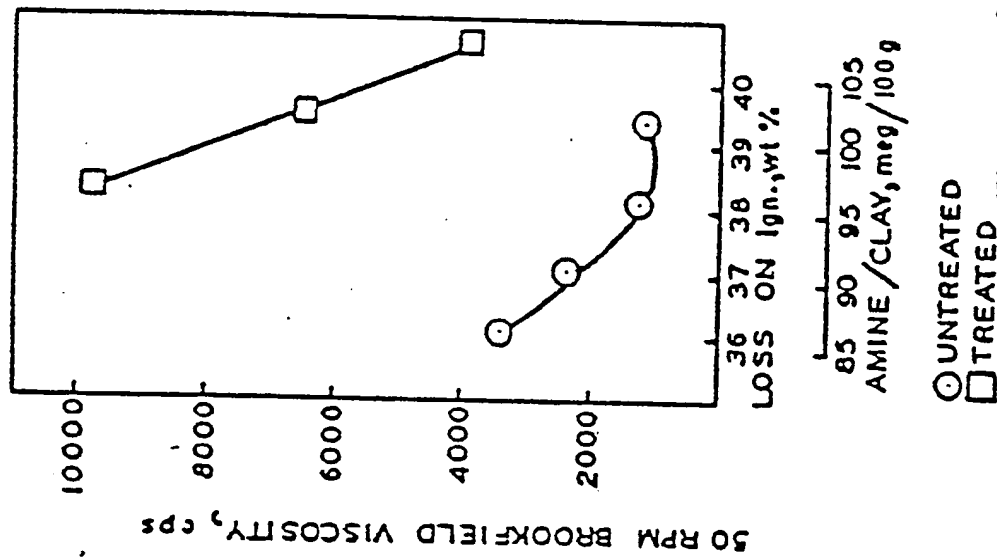


FIG. 9

EFFECT OF TREATMENT OF CRUDE BENTONITE BY HIGH ENERGY PUGMILLING. VISCOSITY MEASURED IN ODORLESS MINERAL SPIRIT GEL.

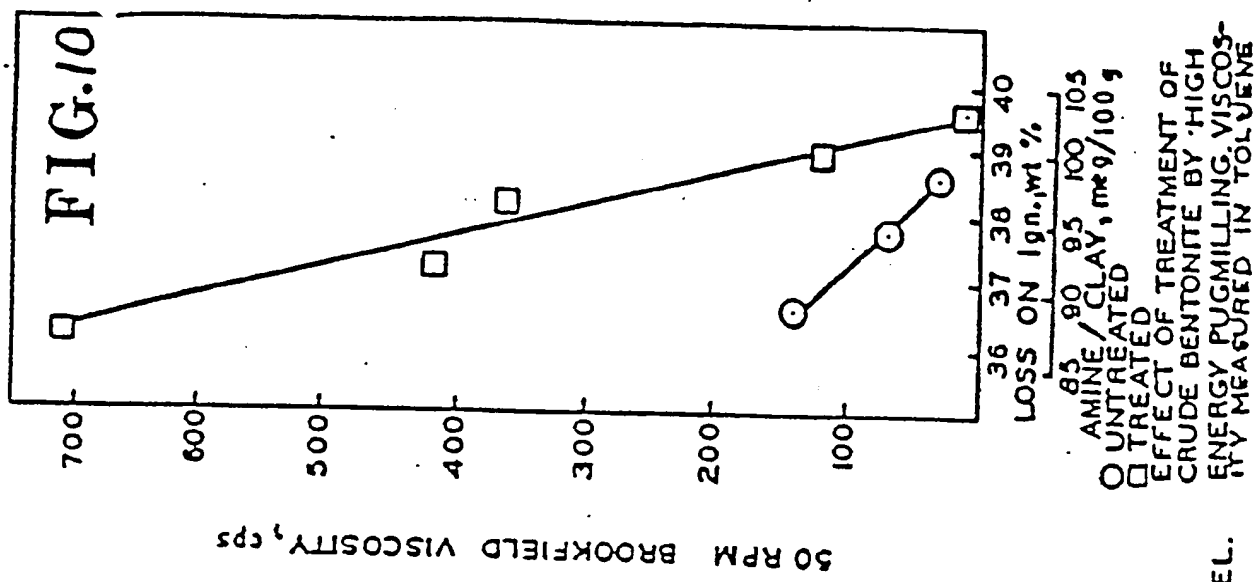


FIG. 10

EFFECT OF TREATMENT OF CRUDE BENTONITE BY HIGH ENERGY PUGMILLING. VISCOSITY MEASURED IN TOLUENE



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
E	EP-A-0 160 514 (ENGLISH CLAYS LOVERING POCHIN & COMPANY LTD.) * Page 7, lines 13-33; page 5, lines 1-11 *	1, 2, 4 6, 7	C 01 B 33/26 C 01 B 33/20
X	FR-A-2 226 360 (LAPORTE INDUSTRIES LTD.) * Page 4, lines 4-5; page 4, lines 22-26; page 5, lines 25-33 *	1	
Y		2-6, 8-12	
X	US-A-4 469 639 (T.D. THOMPSON III et al.) * Examples 5, 7 *	1	
Y		2-6, 8-12	
D, Y	US-A-3 348 778 (M.I. COHN et al.) * Column 6, lines 59-67; column 6, lines 9-41 *	2-6	
Y	US-A-2 206 633 (M.W. DITTO) * Claim 1 *	8	
<div style="text-align: center;">--- -/-</div>			
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19-06-1986	Examiner SCHUT, R. J.
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DOCUMENTS CONSIDERED TO BE RELEVANT			Page 2
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D, Y	US-A-3 574 345 (R.E. BROCHNER) * Claims 1, 7 * -----	9-12	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19-06-1986	Examiner SCHUT, R. J.
CATEGORY OF CITED DOCUMENTS			
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